

Metal Speciation in Contaminated Soil: Complementary Results From Selective Sequential Extractions and XAFS Spectroscopy

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Introduction: Metal-contaminated soils are of high environmental concern in many countries. Prediction of ecotoxicology as well as development of technically and economically feasible remediation strategies requires knowledge on metal speciation. However, soils may consist of a variety of chemical micro-domains, leading to the coexistence of several chemical forms in even small bulk samples. XAFS spectroscopy is well suited to identify the predominant species, but other accessory species may be of equal or even higher importance for the mobility or toxicity of a metal. Therefore, we tested a combination of selective sequential extractions (SSE) and XAFS to identify and quantify multiple species in soil.

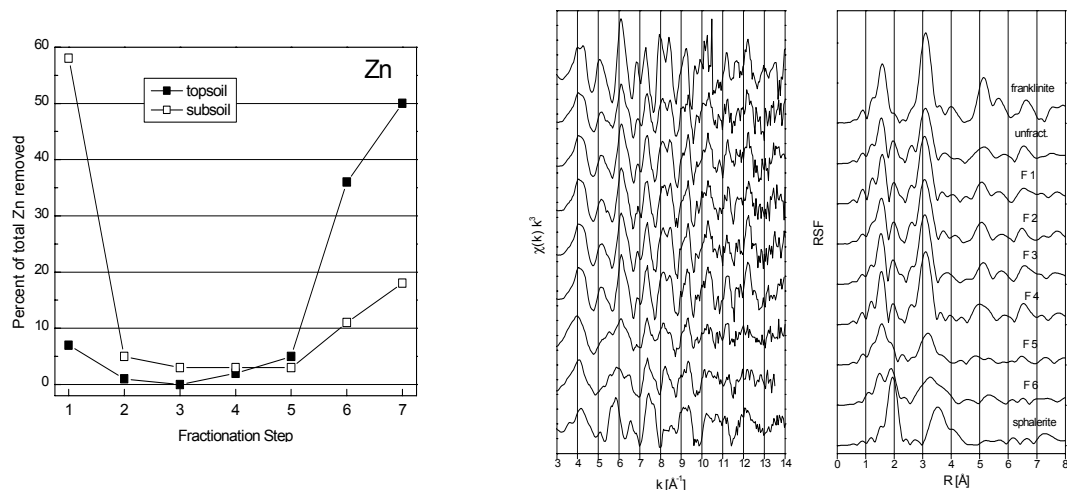
Methods and Materials: Topsoil and subsoil material from the Palmerton superfund site (6000 ppm Zn, 6000 ppm Pb) were sequentially extracted (1). Zn-K edge XAFS spectra of the residuals after each extraction step were collected in fluorescence mode.

Results: We were able to identify both franklinite and sphalerite in the topsoil, which have been deposited during the smelter operation (Fig. 1 and 2). Using principal component analysis, we identified and quantified small amounts of Zn sorbed as outer- and inner sphere sorption complexes in addition to the mineral phases. In the subsoil, most Zn was exchangeable (Fig. 1), while lithiophorite could be identified by XAFS after removing the exchangeable fraction.

The results agree well with those of an earlier study using micro-focused XRF and XAFS spectroscopy (2). The strength of microspectroscopy is in identifying the spatial distribution of metal species, which is important to increase our understanding of, e.g., metal transport along preferential water flow paths or metal uptake by plant roots. The strength of chemical extractions combined with bulk XAFS spectroscopy is the improved identification and quantification of more labile phases.

Several factors led to the better identification and quantification of Zn species, including the successive reduction of metal species by the SSE which eased their subsequent identification by XAFS, the larger number of slightly changing XAFS spectra which could be used for principal component analysis, and the identification of SSE artifacts by XAFS.

- References:** 1. Zeien, H. and Brümmer, G. W., *Mitt. Dtsch. Bodenkundl. Ges.* **66**, 439 (1991).
2. Roberts, D. R., Scheinost, A. C., and Sparks, D. L., *Environ. Sci. Technol.*, in press (2001).



Left: Zn removed from the Palmerton topsoil and subsoil samples by selective sequential extractions. Right: Zn-K-edge XAFS of residuals after each extraction step in comparison with franklinite and sphalerite reference spectra.